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Guidance for Collection of Ambient Non-Methane Organic Compound (NMOC) Data for Use in 1982 Ozone SIP Development, and Network Design and Siting Criteria for the NMOC and NOx Monitors

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16. ABSTRACT

Guidance is given on the selection, siting and use of NMOC monitoring instruments for use in preparing 1982 Ozone SIPs. Some of the commercially available NMOC continuous monitors can provide data useful for modeling and for development of NMOC abatement strategies, if they are carefully maintained and calibrated. Collection of grab samples of ambient air for subsequent analysis by GC methods may be needed if a photochemical model is to be used, but this may be better done by a contractor.

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by

Monitoring and Data Analysis Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

June 1980

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This document has been reviewed by the Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, and approved for publication. Subject to clarification, the contents reflect current Agency thinking.

EPA-450/4-80-011

PURPOSE

The purpose of this document is to provide guidance for collection of ambient non-methane organic compound (NMOC) data and siting of the monitoring instruments. Ambient NMOC data will be needed as input to various photochemical ozone models which may be used for the 1982 ozone SIPs. Special guidance on NMOC monitoring is needed because:

(1) ambient NMOC monitoring has not been previously required, nor is it routinely performed in more than a few areas of the Nation;

(2) NMOC monitoring is needed, not to determine compliance with a NMOC ambient air quality standard, but to aid in control strategy planning activities associated with achievement of the ozone ambient standard;

(3) the nature and extent of NMOC monitoring varies depending on which of several NMOC-O_3 relationships (models) is used for control strategy planning.

(4) NMOC monitoring presents unique problems not generally encountered in monitoring for other criteria pollutants; and,

(5) significant technical, logistical, and other problems exist with currently available NMOC monitoring methodology.

This guideline attempts to explain these circumstances more completely and provide guidance in effectively carrying out an ambient NMOC monitoring program.

BACKGROUND

Prior to the initial setting of National Ambient Air Quality Standards (NAAQS) in 1971, few agencies outside of California performed air monitoring for organic compounds. Even with the setting of the 0.24 ppm NAAQS, to be used as a "guide" toward achieving the former 0.08 ppm oxidant standard, NMHC (or NMOC) monitoring was not required because NMHC* is not a criteria pollutant (health or welfare based standard) for which the NAAQS must be achieved.

In the early to mid-1970s, many State and local agencies began measuring ambient NMOC, despite the fact that such measurements were not required by EPA. Some agencies reported the measured values to the National Aerometric Data Bank (NADB), but the accuracy of the NMOC data has often been questioned because the early NMOC methodology was unreliable. The lack of a NMOC monitoring requirement and the unreliability of the methodology in routine field use prompted a memorandum from OAQPS (in 1975 - copy attached), recommending a moratorium on purchase of new NMOC instruments. This recommendation was based on results of a contractor study of NMOC instrument user experience** and some unpublished work carried out by EPA in North Carolina. Anticipating a subsequent time when NMOC monitoring might be needed, the memorandum recommended that existing NMOC analyzers be retained and that agencies continue to operate such analyzers for trend purposes, if desired. Indeed, some agencies continued to monitor NMOC routinely.

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* Henceforth in this document, non-methane hydrocarbons (NMHC) will be referred to as NMOC, since the various methods of analysis also measure organics other than hydrocarbons.

** EPA-650/4-75-08, December 1974, "Survey of Users of the EPA Reference Method for Measurement of NMHC in Ambient Air"

While there has been little further commercial development of continuous NMOC monitoring instruments since the 1975 memorandum, this is not to imply that nothing has been done in the interim about improving the measurements. An EPA contractor study investigated the fundamentals of FIDs (flame-ionization detector) used in NMOC analyzers, and also compared the responses of various commercial instruments to ambient atmospheres.* In addition, ORD/RTP has maintained a program for evaluating new NMOC measurement methods. ORD/RTP has also attempted to identify the principal reasons for lack of reproducibility of NMOC measurements between various instruments. Unfortunately, due to inherent problems in measuring NMOC, any new measurement techniques which have substantially better characteristics than the present continuous FID method may not be available for several years. On the other hand, some presently available instruments are thought to be capable of yielding acceptable data at concentrations above about 0.5 ppmC if they are carefully maintained and calibrated.

AMBIENT NMOC MONITORING METHODS

Two general categories of NMOC monitoring methods are available: These are a) "continuous" and b) "discrete" or sometimes called "grab sample" analysis.

Continuous Methods

Continuous methods provide hourly average NMOC concentrations, up to 24 per day, at fixed sites. They are somewhat analogous to $NO/NO_2/NO_x$

* EPA-600/4-77-033, June 1977, "Evaluation of the EPA Reference Method for the Measurement of Non-Methane Hydrocarbons - Final Report".

analyzers in that they provide separate measurements of total organic compounds (TOC) and of methane (CH_4). The difference between the TOC and CH_4 measurements is (defined as) the NMOC measurement. Most NMOC analyzers are designed to perform the subtraction automatically and provide a direct NMOC output.

The TOC and CH_4 measurements are made with a FID, but two methods for separating the CH_4 from the TOC are in general use. Chromatographic analyzers use adsorbent columns to separate the CH_4 from all other organic compounds. These analyzers tend to be rather complex, require special operating procedures, and provide up to 12 analyses per hour rather than a truly continuous measurement. Other analyzers use a catalytic process to separate CH_4 by oxidizing all hydrocarbons other than CH_4 in a special controlled-temperature oxidizer. They may be either dual channel, in which the TOC and CH_4 are measured simultaneously, or cyclic, where TOC and CH_4 are measured alternately. Aside from operational complexity, both chromatographic and catalytic types of continuous NMOC analyzers are equally acceptable, subject to the limitations discussed below.

Continuous NMOC analyzers suffer from a number of inherent technical problems which limit the reproducibility of data which they provide. Chief among these is the necessity of subtracting two comparably-sized numbers to obtain a measure of the NMOC. Because the difference between the TOC and CH_4 measurements--i.e., NMOC--is usually considerably smaller than either of the individual TOC or CH_4 concentrations, small errors in the TOC or CH_4 measurements may become large percent errors in the NMOC difference. Furthermore,

ambient TOC and CH_4 concentrations must be measured on broad, relatively insensitive ranges of the instrument in order to accommodate the frequent wide excursions of the TOC and CH_4 ambient concentrations.* Also, FIDs are sensitive to changes in operating conditions such as flow rates, temperature, burner cleanliness, etc., which may result in zero and span drift. These characteristics make careful calibration and accurate balance of the TOC and CH_4 channels imperative. However, with good operational and quality control procedures which include careful attention to gas pressures and frequent zero, span and calibration checks, the analyzers should yield useful measurements at concentrations above about 0.5 ppmC.

Other NMOC analyzer problems over which the operator may have little or no control include measurement of TOC and CH_4 in different samples of air due to sequential, cyclic operation (usually not a problem for hourly averages), non-uniform sensitivity to various organic compounds and from one analyzer design to another, operational complexity, and potential safety hazard from hydrogen gas which all FIDs require.

There is currently no reference or equivalent method for NMOC, nor is one expected in the near term (3-5 years). However, it is recommended that analyzers selected for NMOC monitoring in the next one to two years be of the conventional FID type described above, using either chromatographic or catalytic separation of CH_4. Several such analyzers are currently available from

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* For example, NMOC instruments are usually set to measure full-scale concentrations of TOC of 10 ppm. If the TOC concentration were 5 ppm and the CH_4 concentration were 4 ppm, NMOC would be 1 ppm. Assuming a 10% error in the TOC measurement--0.5 ppm--this would result in a 50% error--1 $\pm$ 0.5 ppm--in the NMOC computations.

manufacturers, such as the Bendix Corporation (Lewisburg, WV), Byron Instrument Co. (Raleigh, NC), Meloy Laboratories, Inc. (Springfield, VA) and Mine Safety Appliances Company (Pittsburgh, PA). In addition, older, out-of-production analyzers such as the Beckman 6800 may be used if still in servicable condition.

The use of a non-conventional NMOC analyzer may be considered, provided its NMOC measurements have been characterized and found to be reasonably relatable to sum-of-species measurements provided by sophisticated GC analysis (see next section) or are otherwise deemed suitable for the application for which the NMOC data will be used. Such non-conventional analyzers might be based on techniques such as direct-reading backflush chromatography, processes which convert all NMOC compounds to CH_4, etc. Additional guidance on the advantages and suitability of these new techniques will be forthcoming from EPA as test, characterization and comparison data for them become available.

"Discrete" or "Grab-Sample" Analysis

More accurate and sensitive NMOC measurements can be obtained by analysis of ambient air samples using a sophisticated, multi-component gas chromatographic (GC) analysis system. The cost and complexity of such a system precludes *in situ* monitoring; hence, ambient air samples must be collected in plastic bags or stainless steel canisters and subsequently analyzed in a laboratory. Furthermore, because of these costs and complexities, analysis of ambient NMOC by this method is limited to short-term (1-2 months) studies rather than year round monitoring. Discrete samples can be collected by integration over a period of one hour or more, or grab samples can be collected in a few seconds. They are transported to the chromatograph and analyzed

within a few hours to minimize losses or contamination from the bag or container.

The analysis yields individual species concentrations of low-to-medium carbon number compounds (C_2-C_{10}) commonly found in ambient air. Individual compounds may be combined into functional groups, such as paraffins, olefins, aromatics, etc., if desired. A simple total NMOC measurement may be obtained by summing the concentrations of the various individual compounds and groups in the sample. This measurement provides accuracy superior to the continuous NMOC measurement, especially at concentrations below 0.5 ppmC. The concentration of individual compounds may be useful information for other air pollution studies, also.

The sophisticated GC analysis of discrete samples and the high level of expertise necessary for these complex procedures are a serious problem which limits the usefulness of this method in routine applications. Such capability cannot be developed in a few weeks, or even months, by an agency or private laboratory. Standardized published techniques are not yet available; thus, skill is acquired only by apprenticeship and experience. Even the number of university or contractor laboratories presently able to perform these analyses competently is very limited.* EPA will attempt to widen contractor support capabilities by the summer of 1981. A guidance document outlining the procedures which should be followed in collecting, handling and analyzing samples has recently been prepared.**

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* Much of the current capability will be utilized in the Northeast Corridor and other studies in the summer of 1980.

** EPA-450/4-80-008, April 1980, Guidance for the Collection and Use of Ambient Hydrocarbon Species Data in Development of Ozone Control Strategies.

CURRENT NMOC MONITORING REQUIREMENTS

Current NMOC ambient monitoring requirements stem entirely from the need to control hydrocarbons as precursors to the photochemical formation of ozone. Recent advancements in the development and verification of quantitative models (e.g., photochemical dispersion models) relating NMOC emissions and NMOC ambient concentrations to photochemical ozone concentrations now allow improved estimation of the degree of NMOC control necessary to achieve the NAAQS for ozone. Thus, NMOC data have become a necessary input to models that are used to develop the ozone NAAQS attainment strategy. Current models (e.g., city-specific EKMA* and sophisticated photochemical dispersion models) require NMOC as input.

Method Applicability

Photochemical dispersion modeling is the most sophisticated type of modeling. Photochemical models require detailed organic species data in order to establish initial and boundary conditions - as well as continuous NMOC data - for trouble shooting and verification of the model in each new application. Organic species data are also needed to check the accuracy of emission inventory estimates in various portions of the modeling region. Grab samples of organic species taken by aircraft are needed as input and to verify organic concentrations aloft in the model.

EKMA requires continuous measurements of the higher NMOC levels in the polluted air mass in the areas of highest precursor emission density. Some

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* Empirical Kinetic Modeling Approach

measure of organic compounds upwind is needed to assess transport into the area if this is thought to contribute significantly to the area's NMOC burden. Because of possible inaccuracies of continuous measurements at lower concentrations, (i.e., < 0.5 ppmC), discrete sampling techniques and the summing of non-methane organic species concentrations are recommended for upwind NMOC measurements.

The NMOC data are to be collected during the season of peak ozone concentrations (summer). NMOC concentrations are often high in central urban locations and at those times of the day (early morning) when accurate measurements are required for the models. Also, NMOC concentrations are most often high on those days when high values of ozone are measured later in the day. Consequently, (with the exception of upwind measurements) NMOC concentrations are more frequently expected to exceed the 0.5-1.0 ppmC threshold where the continuous NMOC analyzer's accuracy is thought to be satisfactory for model needs. Continuous NMOC measurements below 0.5 ppmC may be inaccurate for use in the O_3 models, even when the instruments are operated under the best quality control procedures.

Additional Technical Assistance To Be Available

As noted earlier, errors due to variability with currently available continuous NMOC analyzers are a problem, and limit their usefulness to higher concentration measurements. To minimize these errors and to obtain maximum usefulness of the continuous NMOC data, careful attention to calibration, operational procedures, and quality assurance is necessary. Technical guidance in these areas will be provided in a Technical Assistance Document

(TAD) to be prepared by EMSL at Research Triangle Park, North Carolina. Regional Offices will be notified and supplied copies of this TAD as soon as it is available (expected in November 1980). For NMOC measurements to be made in Summer 1980, interim guidance is given in an appendix to this document.

As the EPA's Environmental Monitoring Systems Laboratory (EMSL) develops guidance on standard calibration procedures, quality assessment and quality control procedures for existing NMOC analyzers, OAQPS plans to develop and to present workshops on this material, as well as video tapes of such workshops, in order to transfer the newly developed procedures and information to State and local agencies in a timely fashion.

General technical guidance on organic species analysis by GC (including recommendations for standardized procedures) has been developed for use by State and local agencies (see Footnote on Page 7). However, it is generally recommended that a competent contractor be sought to carry out this part of the NMOC measurements, rather than for a State or local agency to attempt such a measurement program, particularly if they have not had previous experience with GC techniques.

Another reference source for monitoring guidance for NMOC includes the May 10, 1979, Part 58, Monitoring Regulations. Further, the guidance document, "Site Selection for the Monitoring of Photochemical Air Pollutants," EPA-450/3-78-013, April 1978, provides additional detailed guidance for location of NMOC monitors and classifying spatial scales of representativeness.

FUTURE NMOC MONITORING

Beyond the development of the 1982 SIPs, there will be a continuing need for NMOC ambient monitoring data. Agencies should continue to utilize their NMOC monitors to assess trends in ambient NMOC and ozone levels relative to hydrocarbon emission reductions. This information will provide an additional means (besides ozone trends) to assess the effectiveness of hydrocarbon (and NO_x) control strategies. Also, these trend data will provide further insight into the projection capabilities of the models used.

Under the current SIP surveillance plan requirements, State and local agencies will be conducting ambient monitoring at SLAMS* or NAMS* sites for the various criteria pollutants. In view of the continuing needs for NMOC monitoring, NMOC monitoring may be required as part of the NAMS networks. Thus, analyzers purchased in earlier special monitoring efforts for the 1982 ozone SIPs may eventually be incorporated into the NAMS network, with the resulting data to be submitted to EPA for control strategy evaluation. It is anticipated that Part 58 rulemaking revisions pertaining to NAMS NMOC monitoring would not occur before calendar year 1982. During the time period after a State or local agency has collected NMOC data for the 1982 SIPs, and up until the NMOC revisions to Part 58, it is recommended that control agencies continue operating and submitting NMOC data to EPA.

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* SLAMS State/Local Air Monitoring System

** NAMS National Air Monitoring System

NETWORK DESIGN AND SITING CRITERIA FOR NMOC/NO_x MONITORS

A. General Conclusions

Two general considerations for all sites are recommended before discussing specific criteria.

1. NMOC and NO_x analyzers should be collocated; and,

2. NMOC and NO_x levels and/or ratios should not be predominantly influenced by the emissions from a single street or source.

B. Type and Location of Site

Although the following types of sites are listed in a general priority order, it will be up to each specific user to determine the appropriate number and mix of sites in the development of his individual SIP. Siting recommendations for use in the EKMA model have been made in EPA-450/2-77-021a and EPA-450/2-77-021b.

1. Maximum Emissions Density Site - This site should be located in the area of maximum emissions. Automobile traffic density can be used as a surrogate for NMOC/NO_x emissions. In an absence of traffic density maps, the commercial business district of the urban area may be used to reflect the area of maximum emissions. If there is a predominant summer morning wind direction associated with the area, the downwind fringe of the area of maximum emission density is preferable. If there is no predominant wind direction, the centroid of these areas is preferable. Since the conversion of NMOC/NO_x to oxidants occurs over a wide area and at elevated altitudes, the monitoring site should reflect this, as well, and not merely be representative of the

emissions of a single street. Therefore, the minimum height acceptable for this type of monitoring is 10 meters. Minimum setbacks from roadways will be the same as those found in the Part 58 guidance for NO_2 monitoring sites, except that the setback requirements may be met by horizontal, vertical or slant distance. These setbacks are reproduced in Table 1. Spacing from obstructions is covered in Section C below.

Table 1. Minimum Separation Distance for NMOC/NO_x Stations and Roadways (edge of nearest traffic lane)

Roadway Average Daily Traffic, Vehicles Per Day	Minimum Separation Distance Between Roadways and Stations, Meters
≤10,000	≥10[a]
15,000	20
20,000	30
40,000	50
70,000	100
≥110,000	≥250

[a] Distances Should Be Interpolated Based on Traffic Flow

2. Industrial Source Emissions Site - Although the bulk of NMOC/NO_x emissions comes from transportation sources, some urbanized areas have appreciable emissions from the industrial sector. As with the maximum emission density site, a downwind fringe area would be preferable. The spacing from obstructions, height and setback criteria would be identical to the maximum emission density site, with the additional restriction that the site should not be within 200 meters of the 10^o plume sector from a point source constructed along the prevailing summertime morning wind direction.

3. Upwind Background Site - This site is used in some modeling applications that call for the incoming NMOC/NO_x to be handled differently from the locally generated pollutants. As such, the site should be located 10-35 km upwind of the urbanized area in the most frequent summer wind direction. The site should comply with setback requirements as shown in Table 1. Since the upwind site should not be affected by local sources, the height criteria can be less restrictive. Accordingly, the recommended height is 3-15 meters. The spacing from obstructions is covered in Section C below.

4. Downwind Edge of City Site - This site is located further downwind than the area of maximum emissions and, therefore, has had a chance for more mixing than the maximum emission site. The specific siting criteria should conform to that for the upwind background site.

C. Spacing from Obstructions

Buildings, trees and other obstacles may possibly scavenge NO_2. In order to avoid this kind of interference, the station must be located well away from such obstacles so that the distance between obstacles and the inlet probe is at least twice the height that the obstacle protrudes above the probe. For similar reasons, a probe inlet along a vertical wall is undesirable because air moving along that wall may be subject to possible removal mechanisms. The inlet probe should also be at least 20 meters from trees. There must be unrestricted airflow in an arc of at least 270^{o} around the inlet probe, and the predominant wind direction for the season of greatest pollutant concentration potential must be included in the 270^{o} arc. If the probe is located on the side of the building, 180^{o} clearance is required.

SUMMARY

The following points summarize the guidance related to NMOC data collection for 1982 SIPs:

- NMOC data collection is needed for modeling to support development of 1982 ozone SIPs.
- NMOC monitoring activities will differ, depending upon the type of ozone model to be used for control strategy development. Requirements for use with EKMA are identified in EPA-450/2-77-021a and EPA-450/2-77-021b.
- NMOC data collection should take place during the oxidant season, if not all year.
- Continuous analyzers used for NMOC monitoring in the next one to two years should be of the conventional selective oxidation or chromatographic FID type. New, unconventional NMOC techniques may be considered if characterization data are available to show suitability.
- Continuous monitors provide data useful for modeling at higher concentrations (> 0.5-1 ppmC). Improved maintenance/operating/quality assurance procedures are being developed to provide greater assurance that acceptable data are collected.
- Measurements made with continuous NMOC monitors are generally expected to be useful, since many of them will be made during peak NMOC season, at peak NMOC time during the day, and in the area of peak NMOC emission density when ambient NMOC concentrations are expected to be high.
- Some organic species measurements may also be needed, especially for determining upwind NMOC concentrations and for use in sophisticated photochemical dispersion models if a State chooses to use one of these models.
- NMOC instruments should be collocated with NO_x instruments. Monitoring sites should be carefully chosen in order to minimize undue influence of emissions from single sources.
- Additional guidance is available on:
  - NMOC species data collection (EPA-450/4-80-008);
  - maintenance/operating procedures for continuous analyzers (in preparation - available by November 1980).
- Long-range EPA plans call for considering requiring routine NMOC monitoring at selected NAMS in major metropolitan areas.

APPENDIX

INTERIM GUIDANCE FOR NMOC MEASUREMENTS

NMOC analyzers should be set up and operated according to the manufacturer's instructions. Special attention should be given to matching or balancing the TOC and CH_4 responses, particularly on dual-FID analyzers, so that the CH_4 is accurately subtracted from the TOC (whether done internally by the analyzer or external to the analyzer). Flow rates, as well as other operational parameters, should be measured to assure that they are correct. For chromatographic analyzers, initial and periodic manual chromatograms should be obtained to verify that the gating and operational sequences are properly timed. Also, all maintenance procedures should be carried out according to the manufacturer's instructions.

NMOC measurements should always be reported in ppmC (explained later) and be referenced to a propane standard. This is because FID analyzers respond differently to different organic compounds, and propane provides a response close to the average FID response of the organic compounds in the atmosphere. NMOC measurements referenced to propane are comparable to total NMOC measurements made by GC species analysis and are appropriate for use in EKMA.

The way that NMOC analyzers are referenced to propane differs, depending on the design of the analyzer. Analyzers having a direct NMOC output with an individual span control may be physically calibrated directly with propane. However, the TOC and CH_4 responses may have to be first calibrated

with CH_4 to insure that the CH_4 measurement is correctly subtracted from the TOC measurement. Other analyzers must be calibrated with CH_4. Then the (TOC - CH_4) reading (obtained either from the analyzer or by external subtraction) must be corrected to propane as follows:

$$NMOC = \frac{(TOC - CH_4) - A}{M} ,$$

where M and A are the least squares slope and intercept, respectively, of the analyzer's response to a multipoint calibration with propane after the physical calibration with CH_4.

Familiarization with the instrument is essential to obtain accurate calibration and to avoid unnecessary adjustments that would waste calibration gas mixtures and complicate the procedure.

Cylinders containing compressed gas mixtures of known concentrations of hydrocarbons in air are used for calibration of the analyzer. These concentration standards should be certified by the supplier to be traceable to NBS Standard Reference Materials (SRM) or should be otherwise referenced to such SRM's. NMOC concentrations are expressed in parts per million carbon (ppmC), which is simply the volumetric concentration (ppmV) multiplied by the carbon number (number of carbon atoms per molecule) of the hydrocarbon compound (see example below).

Two separate hydrocarbon standards are generally needed---a CH_4-in-air standard for calibrating and matching the CH_4 and TOC responses, and a propane-in-air standard to calibrate the NMOC response. As an example, the following standards would be appropriate for a 0 to 10 ppmC scale range:

Standard	ppmV	Carbon Number	ppmC	Used to Calibrate
methane in air	8	1	8	CH_4, TOC response
propane in air	3	3	9	NMOC response

A single gas cylinder containing both methane and propane standard concentrations may be used for periodic span checks between calibrations, but such a combined standard will not allow the channel balance to be checked or adjusted. Furthermore, a two component mixture is usually more expensive and may not be as accurate as separate hydrocarbon standards. The following examples are appropriate for combined standards, if this procedure is chosen:

Compound	ppmV	Carbon Number	ppmC
Subtracting Analyzer:			
methane	8	1	8
propane	3	3	9
CH_4 channel response:			8
NMOC channel response:			9
Nonsubtracting Analyzer:			
methane	3	1	3
propane	2	3	6
Total			9
CH_4 channel response:			3
TOC channel response:			9

All methane standards should be specified to have less than 0.1 ppmC total of other hydrocarbons as impurities. Absence of hydrocarbon impurities is

important for precise analyzer balance and accurate calibration; all methane standards should be checked for impurities before use.

Calibration concentrations may be provided directly by gas cylinders containing the appropriate concentration levels. For multi-point calibration, a separate cylinder is needed for each concentration level.

Greater economy can be realized by obtaining calibration concentrations by dilution, since many different concentration levels may be provided from a single standard cylinder, and consumption of the standard is greatly reduced. In this case, the standard should have a concentration level of several hundred ppmC. An ample source of clean, hydrocarbon-free zero air is, of course, required. The dilution system must have suitable means to control and accurately measure the flow rates of the standard and the zero air, and the two flows must be thoroughly mixed.

All calibration gases should be introduced into the analyzer at atmospheric pressure through the sample inlet. This can be facilitated by installing a "tee" fitting between the analyzer sample inlet and the calibration source, with one leg of the tee left open to the atmosphere as a vent. The flow of calibration gas must exceed the flow demand of the analyzer at all times, with the excess released at the atmospheric pressure vent. This atmospheric vent flow should be about 20 to 50% of the analyzer flow to assure adequate venting without excessive waste of calibration gas. Additional guidance or more specific information on the operation of NMOC analyzers may be obtained from EMSL, Research Triangle Park, NC by calling (919) 541-3791 (FTS 629-3791) or (919) 541-2622 (FTS 629-2622).

A-1

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

SUBJECT: The Unreliability of Non-Methane Hydrocarbon Analyzers and its Impact on HC/O_x Strategies

DATE: 12 MAY 1975

FROM: B. J. Steigerwald, Director
Office of Air Quality Planning and Standards (MD-10)

TO: Roger Strelow, Assistant Administrator
for Air and Waste Management

Surveillance and Analysis Division Directors, Regions I-X
Air and Hazardous Materials Division Directors, Regions I-X

Recent studies with commercial non-methane hydrocarbon (NMHC) analyzers have established the fact that these instruments yield unreliable data. Not only do instruments from different manufacturers produce different results, even instruments from the same manufacturer, with supposedly the same characteristics, yield data sometimes differing by a factor of two. (For comparison, measurements made with different SO_2 instruments have a correlation coefficient of better than 0.85). These studies were carried out by EPA laboratories as well as contractors, and the results are thus thought to be conclusive.

In an attempt to identify the source of trouble, one of the NERC/RTP laboratories is contracting for a 15 month study of the NMHC instrumental technique. At this time, it is thought that the solution lies in rigid specification of the design and construction of the NMHC analyzer as well as a strict protocol for its operation. The contractor will submit his report about January 1977. In the meantime, however, the consequences of these studies and the distant solution cause EPA concern in the following areas:

1. The doubt cast on the Appendix J curve.

2. The enforced delay in possibility of developing area-specific upper limit HC/O_x curves.

3. The validation of HC/O_x models.

4. The lack of knowledge about true NMHC concentrations and their trends in urban areas.

All of these are interrelated, of course. Accepting the situation as it exists, EPA's position on these areas of concern should be as follows:

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Any doubt which may arise concerning the Appendix J curve is misplaced. Data used to construct Appendix J did not come from these instruments--rather, from total hydrocarbon measurements, in general. Under any circumstances, there is an abundance of evidence from many other experimental programs showing a relation between ambient hydrocarbons and photochemical oxidants. Thus, despite the acknowledged deficiencies in the Appendix J curve, it should still be used where appropriate in HC/O_x reduction strategies.

A better relation may exist between non-methane hydrocarbon and ozone, but the data are not available. There is reason to believe, too, that such a relation differs from one metropolitan area to another. We had hopes of constructing area-specific Appendix J-like curves and using these to better define required hydrocarbon emission reductions for the various areas. We believe the idea is still a good one, but we suggest delaying its implementation until we have reliable NMHC data from good instruments.

Most of our laboratory work and field studies on HC/O_x relations are not affected by this discovery of the faulty NMHC instrumental method. Usually gas chromatographic procedures were used which are accurate for specific hydrocarbons. It is only when ambient hydrocarbon measurements are made by the NMHC technique that we lose accuracy.

As you know, NMHC measurements are not required from the states at the present time. In forthcoming revisions to 40 CFR 51.17, we had considered requiring those metropolitan areas where ozone concentrations are estimated to be above the NAAQS in 1977 to begin monitoring for NMHC. This requirement has now been deleted from the draft regulation but will be reconsidered at the appropriate time.

It is our belief that the reference method for NMHC, detailed in 40 CFR 50.10 Appendix E, does not need to be rescinded at this time, however, both because it never had the force of being a required procedure for a criteria pollutant and also because the basic procedure may still be valid. The specifications may just need to be tightened up. Only after the EERC/RTP experimental program has been completed will we know whether it is necessary.

For those agencies which already have NMHC analyzers, it is debatable whether or not their use should be continued. Perhaps the trend data would be interesting. However, it is improbable that past or present values have the required accuracy for any absolute meaning at this time. On the

other hand, this is not to say that the instruments should be junked. Depending on what is found within the next few months, it may be possible to modify present instruments to make their measurements meaningful. However, we certainly cannot encourage the purchase of new NMHC analyzers at this time.

This memo has addressed only the subject of ambient NMHC analyses. Neither mobile source testing nor stationary source testing is affected by this discovery of unreliable data from these instruments since other analytical methods are used.

In summary, because of design differences between various NMHC analyzers, data from these instruments are unreliable. The questioned accuracy of the data obtained from such instruments should in no way discredit the belief that hydrocarbons are a major factor in the generation of photochemical oxidants. Irradiation chamber studies, as well as ambient measurements using gas chromatographic techniques, which do provide accurate hydrocarbon data, have documented the role of hydrocarbons in smog reactions.

cc: D. Borchers